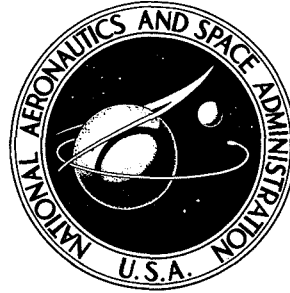


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ENHANCEMENT OF OXIDATIVE VAPORIZATION
OF CHROMIUM (III) OXIDE
AND CHROMIUM BY OXYGEN ATOMS

*by George C. Fryburg, Fred J. Kohl,
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16. Abstract Rates of oxidative vaporization of Cr_2O_3 were found to be markedly enhanced in the presence of O atoms. Investigations were conducted over the temperature range 470 to 1520 K. For Cr_2O_3 the enhancement was about 10^9 at 820 K in oxygen containing 2.5 percent atoms. Rapid oxidative vaporization of bare chromium was observed below 1070 K, the rate being about one-half that of Cr_2O_3 . Results are interpreted in terms of thermochemical analysis.					
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SUMMARY

The oxidative vaporization of chromium (III) oxide (Cr_2O_3) is markedly enhanced by oxygen (O) atoms over the entire temperature range of this study: 470 to 1520 K. The rates maximize at 820 K. This is explained on the basis that $\text{CrO}_3(\text{g})$ volatilized in polymeric form at low temperature and as the monomer above 1070 K.

In the range 470 to 1070 K the O atom reaction is described by the equation $\text{Cr}_2\text{O}_3(\text{s}) + \text{O}(\text{g}) \rightarrow (\text{CrO}_3)_n(\text{g})$ where $n = 3, 4$, and 5. This reaction proceeds with a small activation energy: about 33 kJ mole^{-1} . We were not able to measure the order of the reaction because of complications arising from the rapid removal of the Cr_2O_3 scale in this temperature region.

In the range 1170 to 1520 K, and probably at higher temperatures, the O atom reaction is described by the equation $(1/2)\text{Cr}_2\text{O}_3(\text{s}) + (3/2)\text{O}(\text{g}) \rightarrow \text{CrO}_3(\text{g})$. This reaction proceeds with a low activation energy of 2.4 kJ mole^{-1} and exhibits a $3/2$ order with respect to oxygen atoms. Comparison of the "oxidation probabilities" of the O atoms in this reaction with those of the O_2 molecules in the analogous reaction indicates that the O atoms are 10^4 times more reactive than the molecules at 1220 K and are 10^2 times more reactive at 1520 K.

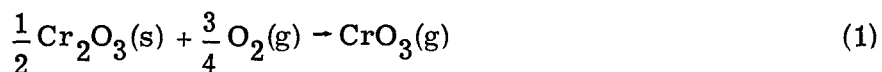
Our rates for the oxidative vaporization of Cr_2O_3 have been compared with rates calculated from thermodynamic equilibrium data. The calculated rates are in qualitative agreement with the experimental rates, indicating a large enhancement and displaying a maximum in the rate at intermediate temperatures. However, the calculated rates are higher by a factor of 10^2 to 10^6 , depending on temperature. We feel the discrepancy arises from the fact that the concentration of O atoms on the sample surface is much less than the equilibrium value corresponding to the gaseous partial pressure, because of the rapid recombination of the O atoms on the hot surface.

We have shown that a rapid, direct oxidative vaporization of chromium metal occurs in the presence of O atoms from 470 to 1070 K. The rates also maximize at 820 K (for the same reason as for Cr_2O_3) and are about one-half the rates exhibited by $\text{Cr}_2\text{O}_3(\text{s})$. The reaction is described by the equation $\text{Cr}(\text{s}) + \text{O}(\text{g}) \rightarrow (\text{CrO}_3)_n(\text{g})$ where $n = 3, 4$, and 5. The process has an activation energy of 29 kJ mole^{-1} and is first order with respect to O atoms. These results are very similar to results obtained for the reaction of O atoms with molybdenum and tungsten. However, the reaction with chromium occurs at much lower temperatures. In addition, the oxidation probability for the O atom in the chromium oxidation is roughly a factor of 10 less than in the molybdenum and tungsten oxidations, the highest value being $\epsilon_{\text{O}} = 0.014$.

INTRODUCTION

Some years ago Fryburg demonstrated that oxygen atoms caused a marked enhancement in the rate of oxidation of platinum (refs. 1 and 2). Subsequently, Rosner and Allendorf (ref. 3) extended these studies to molybdenum and tungsten, obtaining similar enhancements in the rates of oxidation. Madix and Susu (ref. 4), using atomic beam techniques, found an enhanced oxidation of germanium and silicon with oxygen atoms. All these metals form volatile oxides in the temperature range in which the enhanced oxidation was discovered.

This report describes the enhancement, by oxygen atoms, of the oxidative vaporization of an oxide; namely, Cr_2O_3 . The normal oxidation reaction is represented by the equation



In oxygen, at reduced pressures, this oxidative vaporization is detectable above roughly 1170 K, as shown in a recent report (ref. 5). In partially atomic oxygen, the rate is enhanced so markedly that oxidation is readily measured down to 470 K. We have determined the rate of oxidative vaporization of Cr_2O_3 in partially atomic, flowing oxygen at a total pressure of 15.3 N m^{-2} (0.115 torr)¹ from 475 to 1520 K. The experimental rates were corrected by the method given in reference 5 to give "reaction controlled" rates. Oxidative vaporization rates were also calculated from the equilibrium thermodynamic data for comparison.

During the course of this investigation we observed, below 1070 K, a direct oxidative vaporization of chromium metal by the oxygen atoms. This has also been noted by Dickens and Sutcliffe (ref. 6). As a result, measurements were also made of the rate of oxidative vaporization of electropolished chromium in partially atomic oxygen.

EXPERIMENTAL PROCEDURE

The main features of the experimental arrangement and the procedures used in this investigation are described in reference 5. Samples were prepared from a chromium - 0.1-weight-percent-yttrium alloy. The apparatus is shown schematically in figure 1. In the present experiments the oxygen was dissociated by a 100-watt, 2450-megahertz microwave power supply with a slotted wave guide. The amount of dissociation in the region of the oxidation sample was determined with a platinum resistance thermometer,

¹This pressure was the optimum for O atom production.

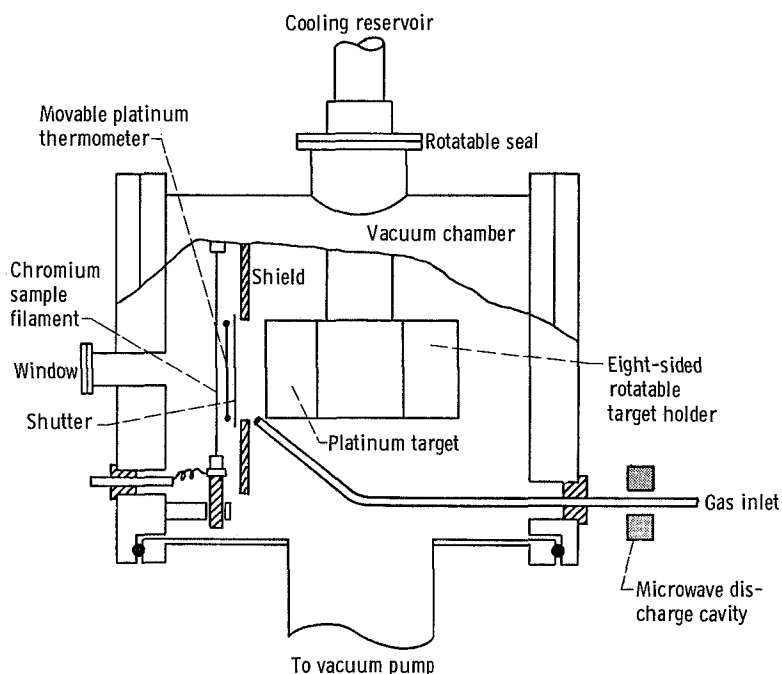


Figure 1. - Schematic diagram of experimental apparatus.

similar to one used previously (ref. 1), that could be moved directly in front of the specimen in the flowing stream of oxygen. The sensing element of this thermometer was made from platinum ribbon 0.025 millimeter thick, 0.25 millimeter wide, and 3 centimeters long. The central 2 centimeters was tapped off with 0.025-millimeter-diameter wires for potentiometric readings. The platinum ribbon was operated at 1173 K, a temperature at which the recombination coefficient for O atoms is close to 1 (refs. 7 and 8).

The percentage of O atoms in the oxygen can be obtained from the measured joule heating resulting from the recombination of the atoms, when the heat of recombination and the pressure of the oxygen are known (see ref. 1 for details). Corrections² were made for the heating resulting from $O_2(^1\Delta_g)$ that are also formed in the discharge (refs. 9 and 11).

²Auxiliary experiments were run in which a long silver ribbon was placed in the gas inlet tube, just downstream from the discharge. This effectively removed all the O atoms, as indicated by blackening of only the upstream end of the silver (ref. 9). The blackening results from formation of AgO (ref. 10) by the O atoms. The residual heating, caused by the $O_2(^1\Delta_g)$ in the gas, was found to be 10 percent of heating obtained without the silver ribbon. This percentage remained the same with or without the nitrogen addition to the oxygen.

Research-grade oxygen was used. This gas contained less than 1 ppm of water vapor,³ so it was necessary to add 5 percent of nitrogen (also research grade) to the oxygen to produce a more useful concentration of O atoms. With the nitrogen added, we obtained about 2.5-percent O atoms at the sample, and with the pure oxygen we obtained about 1.2 percent.

The procedure for conducting experiments was similar to that described in reference 5. For Cr₂O₃ oxidations the chromium ribbons were all preoxidized at a high temperature: 1370 to 1570 K. This was done, as before, in situ for 1/2 hour in the flowing oxygen at 15.3 N m⁻² (0.115 torr), and the thickness of Cr₂O₃ scale formed was 0.01 millimeter (0.4 mil) or greater. The temperature of the specimens was obtained from the reading of the thermocouple spot welded onto the back. This was checked with the micro-optical pyrometer at the higher temperatures.

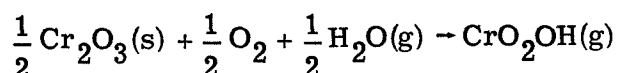
In addition, it was necessary to stabilize the discharge before the oxidations could be performed. The first stabilization of the day required 30 minutes run-in time to obtain constant O atom output. If the arc was shut off during the day, 5 to 10 minutes run-in was sufficient. During these arc stabilizations the shutter was kept closed so that the specimen was not exposed to any atoms. The O atom output was very stable after the initial run-in and was reproducible from day to day as long as the oxygen inlet tube remained clean. Over long periods of time it dropped slowly. Periodically, the inlet tube was removed and cleaned in 5-percent HF followed by copious rinsing with distilled water.

The oxide condensate formed in these experiments was always readily soluble in water, and we have assumed it was CrO₃ based on the reasoning used in reference 5. As before, the water solutions were analyzed for chromium by atomic absorption spectroscopy.

THERMOCHEMICAL PREDICTIONS

Equilibrium thermochemical diagrams have proven useful in describing the chemistry of oxidation and vaporization for many metal - metal oxide - oxygen systems (refs. 13 to 18). We have shown previously (ref. 5) that the thermodynamic description could also be correlated with the kinetic behavior for the oxidative vaporization of a

³The water vapor in the oxygen was maintained as low as possible to prevent complications from the reaction (ref. 12)



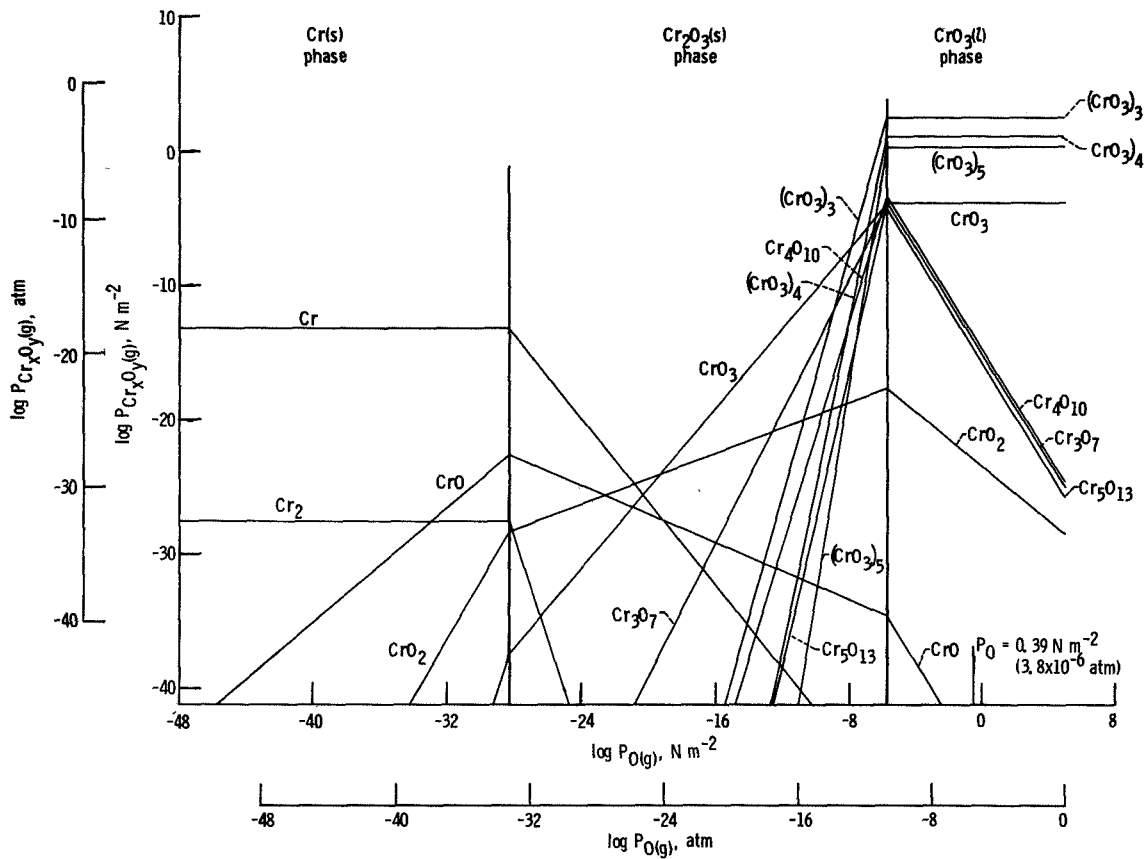


Figure 2 - Equilibrium thermochemical diagram for the chromium - atomic oxygen system at 800 K.

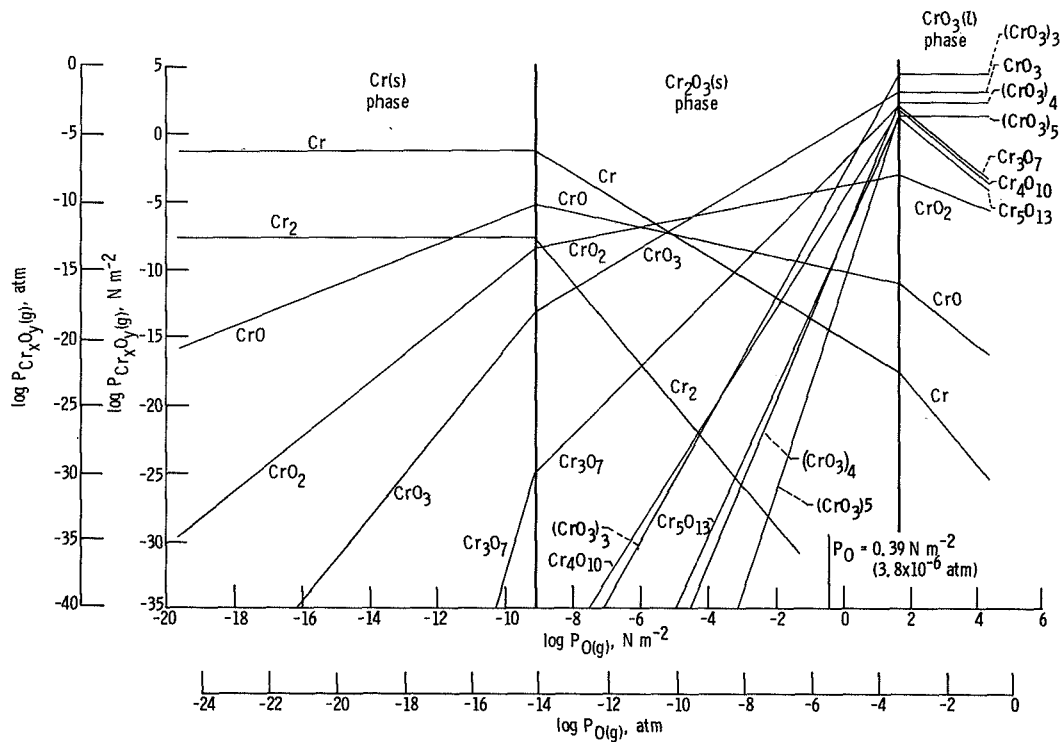


Figure 3 - Equilibrium thermochemical diagram for the chromium - atomic oxygen system at 1500 K.

condensed-phase metal oxide, Cr_2O_3 , reacting with molecular oxygen. Here we will extend the use of thermochemical diagrams to provide a description of the oxidative vaporization of condensed-phase chromium and Cr_2O_3 reacting with atomic oxygen. The effect of adding atomic oxygen is equivalent to increasing the chemical potential of oxygen.

Thermochemical diagrams for the chromium - atomic oxygen system at 800 and 1500 K are given in figures 2 and 3, respectively. (Details of the method of construction and the sources of thermodynamic data are given in the appendix.) For comparison we give a diagram for the chromium - molecular oxygen system at 800 K in figure 4. A similar diagram at 1500 K is given in figure 5.

The atomic oxygen thermochemical diagrams differ markedly from those for molecular oxygen in several respects. In addition to Cr and Cr_2O_3 condensed phases, a CrO_3 condensed phase is present at high oxygen atom pressures. The complex chromium-oxygen molecules are relatively unimportant in the molecular oxygen case. However, the polymeric $(\text{CrO}_3)_n$ and $\text{Cr}_n\text{O}_{3n-2}$ molecules ($n = 3, 4$, and 5) are the predominant species in the vapor phase at high oxygen atom pressures, particularly over the CrO_3 phase. In addition, the actual vapor pressures of the oxides are markedly higher in the atomic oxygen case. At 800 K, comparison of the vapor pressure of $(\text{CrO}_3)_3$ under our O atom partial pressure P_{O} of 0.39 N m^{-2} ($3.8 \times 10^{-6} \text{ atm}$) (fig. 2) with the vapor pressure of CrO_3 under our molecular oxygen partial pressure P_{O_2} of 15.3 N m^{-2} ($1.51 \times 10^{-4} \text{ atm}$) (fig. 4) indicates an enhancement in oxide vapor pressure of about 10^{13} . The oxidative vaporization rate should be enhanced by a similar factor. At 1500 K the situation is a little different. Under our O atom concentration (fig. 3), the polymers of CrO_3 are not stabilized at this higher temperature and the main oxide product is again the monomer, CrO_3 . Comparison of the vapor pressure of CrO_3 from figure 3 at $P_{\text{O}} = 0.39 \text{ N m}^{-2}$ ($3.8 \times 10^{-6} \text{ atm}$) with the vapor pressure from figure 5 at $P_{\text{O}_2} = 15.3 \text{ N m}^{-2}$ ($1.51 \times 10^{-4} \text{ atm}$) indicates an enhancement of about 10^2 .

It is instructive to plot the vapor pressures of the various oxide species against reciprocal temperature T^{-1} for our O atom partial pressure, $P_{\text{O}} = 0.39 \text{ N m}^{-2}$ ($3.8 \times 10^{-6} \text{ atm}$), as presented in figure 6. The polymers of CrO_3 are stabilized over $\text{CrO}_3(l)$ and are the principal vapor species to the Cr_2O_3 - CrO_3 phase boundary at a temperature around 1220 K. At temperatures above this, the pressure of the polymers decreases dramatically and the monomer of CrO_3 becomes the most abundant oxide species, as in molecular oxygen. Because the rate of oxidative vaporization should vary with the vapor pressures, we conclude that the rate in O atoms should increase with temperature to 1220 K and then fall abruptly with increasing temperature.

For comparison with our corrected experimental rates of oxidative vaporization of Cr_2O_3 , we calculated rates from the oxide vapor pressures obtained from the thermochemical diagrams by using the Hertz-Langmuir equation, as in reference 5. However,

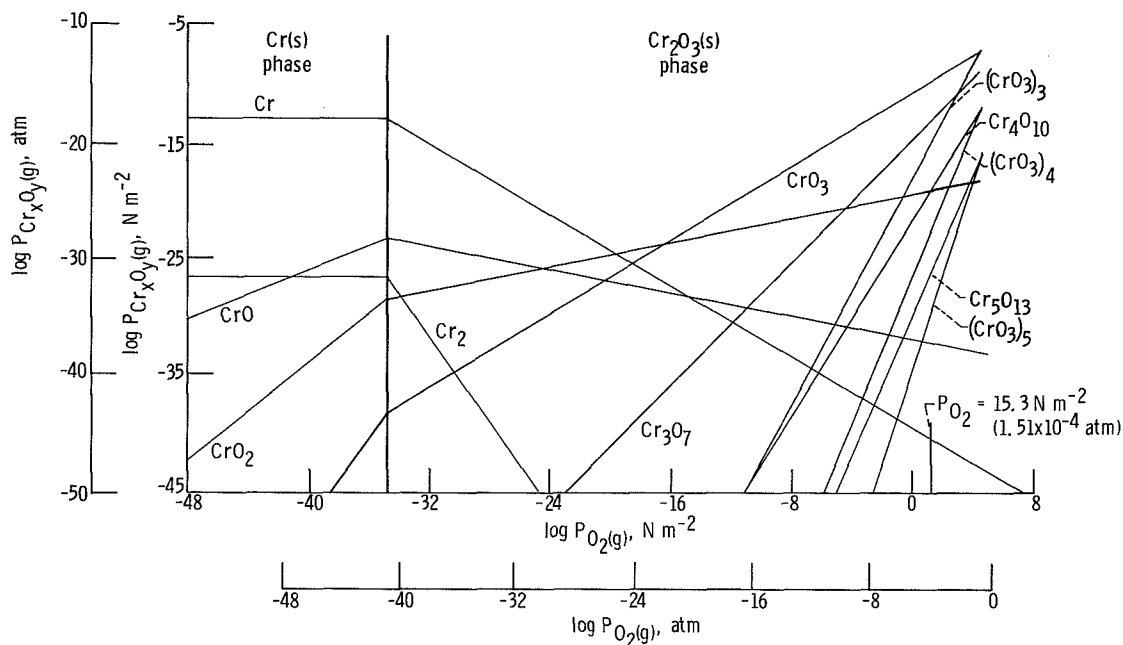


Figure 4. - Equilibrium thermochemical diagram for the chromium - molecular oxygen system at 800 K.

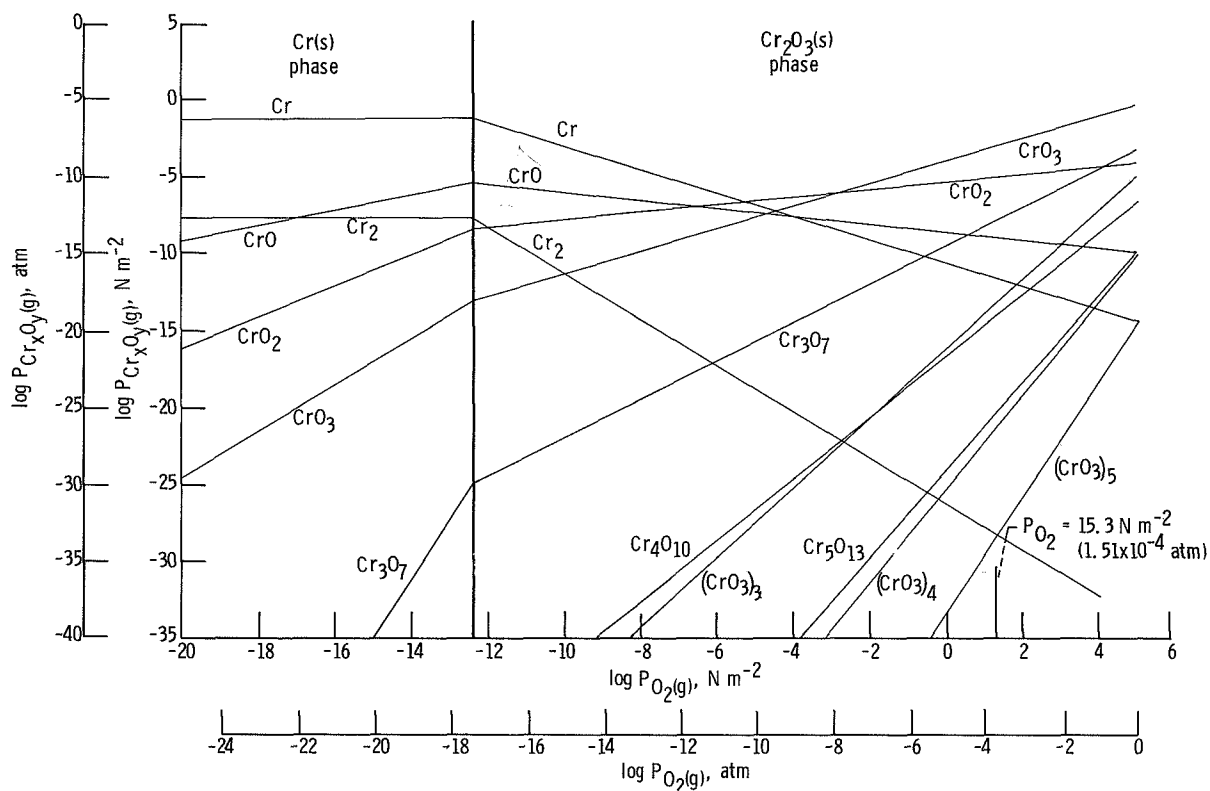


Figure 5. - Equilibrium thermochemical diagram for the chromium - molecular oxygen system at 1500 K.

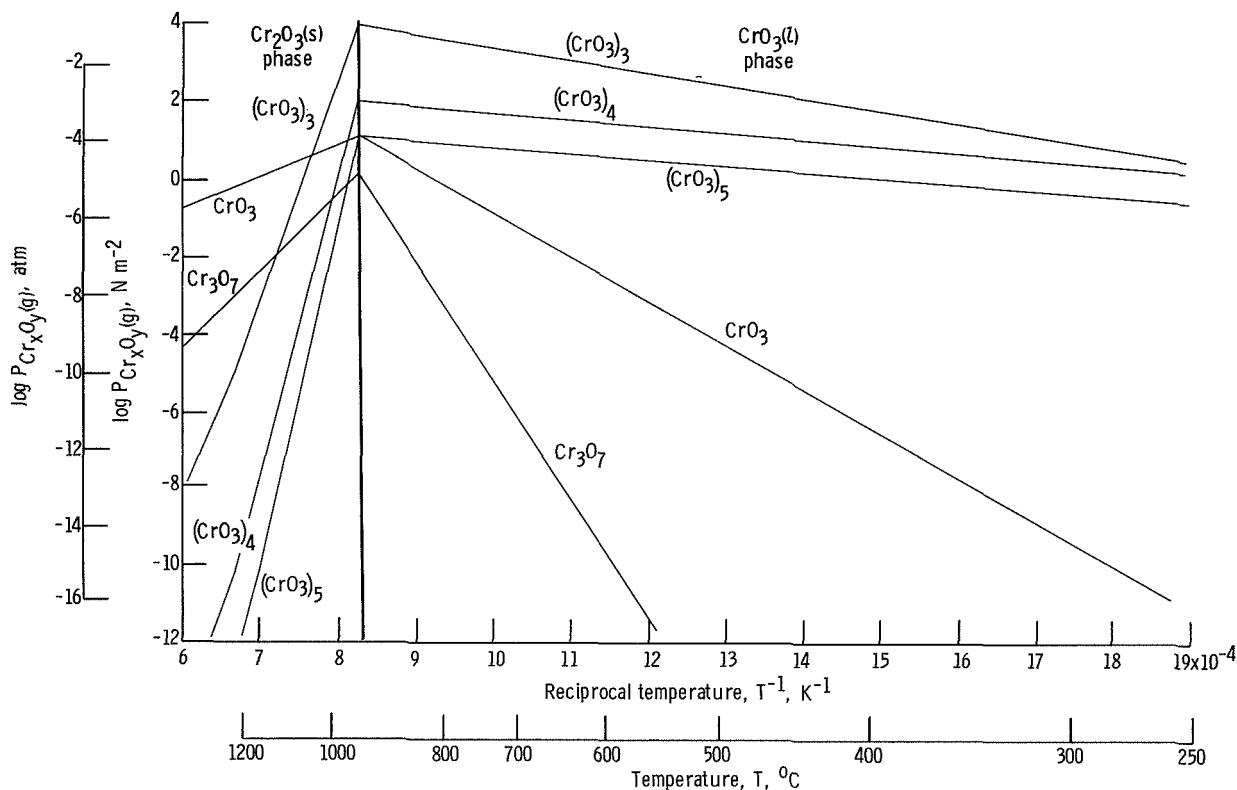


Figure 6. - Equilibrium vapor pressures of various oxide species of the chromium - atomic oxygen system as a function of reciprocal temperature under an oxygen atom partial pressure of 0.39 N m^{-2} ($3.8 \times 10^{-6} \text{ atm}$).

in this case, more than one oxide species were significant. Therefore, rates were calculated for each species and the individual rates summed to give the total rate of oxidation.

RESULTS AND DISCUSSION

General

The rates of oxidation presented in this report have been corrected for a "geometrical factor" and a "diffusion-limitation factor" (escape fraction), as described in reference 5. No corrections have been made for the fact that the diffusing CrO_3 moiety may change with temperature, exhibiting slightly different diffusivities. This would be a secondary effect. All rates reported herein were obtained with an oxygen flow rate of $5 \times 10^{-3} \text{ m}^3 \text{ hr}^{-1}$ (STP) and a pressure of 15.3 N m^{-2} (0.115 torr) in the main chamber. Turning on the microwave discharge to produce atoms had negligible effect on the pressure.

The rates of oxidation of Cr_2O_3 measured at different temperatures in oxygen containing 2.5 percent O atoms are shown in figure 7 (upper solid curve). Also shown for

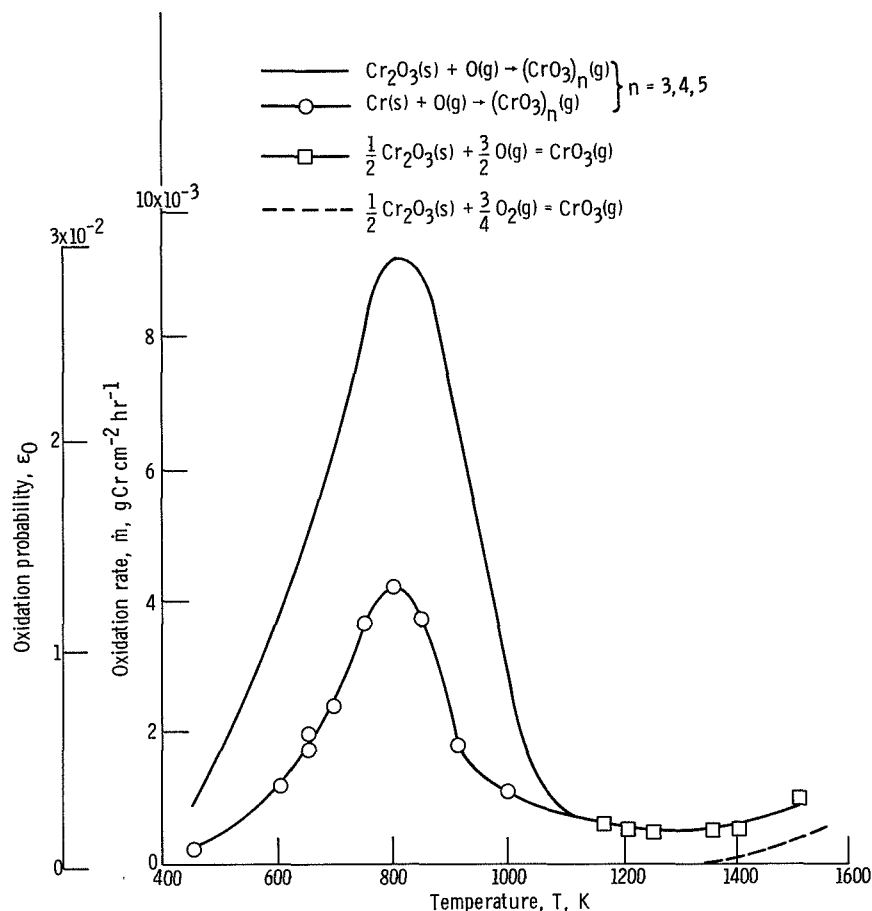


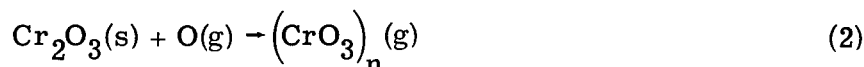
Figure 7. - Oxidative vaporization of Cr_2O_3 and chromium in partially atomic oxygen. Oxygen atom concentration, 2.5 percent; total oxygen pressure, P_{O_2} , 15.3 N m^{-2} (0.115 torr).

comparison are rates of oxidation of Cr_2O_3 in molecular oxygen (dashed curve), which vary from $0.5 \text{ mg cm}^{-2}\text{hr}^{-1}$ at 1570 K to $0.005 \text{ mg cm}^{-2}\text{hr}^{-1}$ at 1270 K . Obviously, the rate of oxidation of Cr_2O_3 has been greatly enhanced by the small concentration of O atoms. Rapid oxidation rates, nearly $10 \text{ mg cm}^{-2}\text{hr}^{-1}$, were observed in the region around 820 K .

Unexpectedly, a rapid, direct oxidative vaporization of chromium metal was observed below about 1070 K . This vaporization occurs partly because of the rapid removal of the Cr_2O_3 by the O atoms at temperatures at which Cr_2O_3 can reform only slowly. Consequently, rates of oxidation of electropolished chromium were also determined and these results are shown in the lower solid curve of figure 7.

It is informative to express the oxidation results in terms of the "oxidation probability"⁴ of the O atoms ϵ_O . These have been calculated from the rates and the measured flux of O atoms and are presented in figure 7. The maximum values of ϵ_O , which occur at 820 K, are 3×10^{-2} for Cr_2O_3 oxidation and 1.4×10^{-2} for the Cr oxidation. In the high-temperature region (1220 to 1520 K), $\epsilon_O = 2 \times 10^{-3}$ for the Cr_2O_3 oxidation.

The peculiar temperature dependence of the Cr_2O_3 rates displayed in figure 7 is similar to that predicted from thermochemical diagrams. We believe it arises from the fact that the O atoms stabilize the polymers of CrO_3 at the lower temperatures and that the oxidative vaporization reaction proceeds by means of the reaction



where $n = 3, 4$, and 5 . That is, the CrO_3 evaporates as fast as it is formed by the oxidation reaction, and in polymeric form. However, at 820 K the polymers apparently become unstable on the surface of the specimen and have difficulty forming. As the temperature increases, the probability of formation decreases. The rate drops because the monomer cannot evaporate at this low temperature. Evaporation of the monomer becomes significant only above 1070 K, and above this temperature the oxidative vaporization proceeds by means of the reaction



The rates for chromium (lower solid curve in fig. 7) display the same type of temperature dependence (from 470 to 1070 K), and the same explanation would apply to these data. The oxidation, in this region, is represented by the reaction



where $n = 3, 4$, and 5 .

⁴The oxidation probability as used by Rosner (ref. 3) is a dimensionless reaction probability defined as the ratio of the flux of metal atoms (regardless of their chemical state of aggregation) away from the reacting surface to the collision flux of $\text{O}(\text{g})$ with the surface.

Oxidation of Cr_2O_3

Results in temperature range 470 to 1070 K. - The rapid removal of the Cr_2O_3 from the preoxidized chromium observed in this temperature region resulted in rates that were time dependent even though one would expect time-independent rates for this type of reaction that should follow linear kinetics. This result was especially noticeable around 820 K. A series of 1-minute runs at this temperature yielded a rapidly decreasing rate that leveled off at a value equal to that of the electropolished chromium (lower curve fig. 7). Therefore, individual experimental values have not been given for the rates of oxidation of Cr_2O_3 in the range 470 to 1070 K. The upper curve (fig. 7) represents the maximum values observed and should correspond to the rate for a thick layer of Cr_2O_3 on the chromium substrate. The oxidation process occurring in this temperature region is represented by reaction (2); namely, $\text{Cr}_2\text{O}_3(\text{s}) + \text{O}(\text{g}) \rightarrow (\text{CrO}_3)_n(\text{g})$, where $n = 3, 4$, and 5.

Because of the semi-quantitative nature of the Cr_2O_3 results in this lower temperature region, it was not possible to determine the order of this reaction with respect to O atoms. However, an Arrhenius plot of the results in the region 470 to 820 K, presented in figure 8, indicates that the reaction is occurring with a small activation energy.

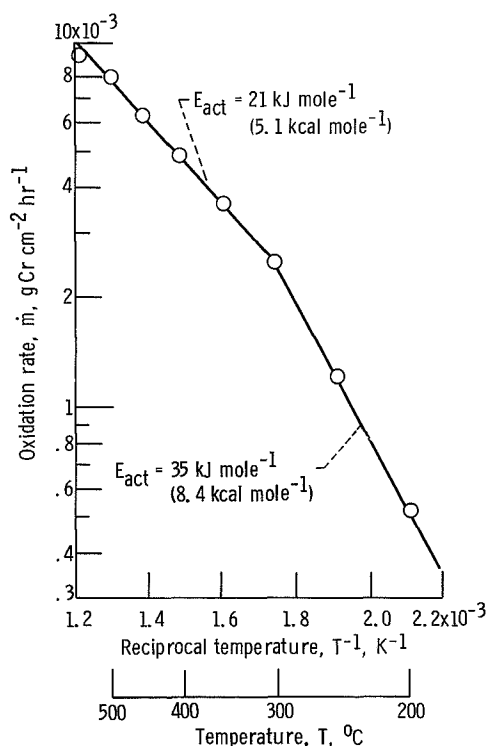


Figure 8. - Arrhenius plot of oxidative vaporization of Cr_2O_3 in partially atomic oxygen from 470 to 820 K. Total oxygen pressure, P_{O} , 0.39 N m^{-2} ($3.8 \times 10^{-6} \text{ atm}$).

The points in figure 8 were taken from the smoothed curve presented in figure 7 (upper solid curve) and obviously do not give a linear curve on the Arrhenius plot. We have drawn two straight lines through the data merely for the purpose of calculating the activation energies. The lower temperature value, 35 kJ mole^{-1} ($8.4 \text{ kcal mole}^{-1}$), was probably less affected by the rapid removal of Cr_2O_3 and is probably the more reliable value. In any event, both values are small and in the range observed for metal - oxygen atom reactions (refs. 2 and 3).

Results in temperature range 1170 to 1520 K. - Above 1170 K the reported rates of oxidation of Cr_2O_3 in O atoms were time independent and not complicated by removal of Cr_2O_3 . The rate of removal of Cr_2O_3 was less in this region, and the rate of formation by oxidation of the underlying chromium by normal oxygen was greater. We did, however, observe a temperature hysteresis effect in this temperature regime. Runs repeated at a given temperature were higher than previously if the specimen had been oxidized at a higher temperature in the time intervening. The effect appeared to be caused by a greatly increased roughening of the oxide surface which occurred around 1470 K and/or by a greater thickness of oxide scale that formed at the higher temperatures. In any event, the rates in this temperature regime were obtained from specimens that were all preoxidized at 1570 K. This procedure eliminated the temperature hysteresis effect.

The oxidation process in this temperature region is represented by reaction (3); namely, $\text{Cr}_2\text{O}_3(\text{s}) + \text{O}(\text{g}) \rightarrow \text{CrO}_3(\text{g})$. The rates of this reaction appear to be independent of temperature from 1220 to 1520 K (fig. 7). They are nearly constant to 1370 K, above which temperature they increase because of the addition of oxide from the oxidation by oxygen molecules. The two simultaneous reactions seem to be additive and independent of each other.

Results of detailed studies of the rates in this region are shown in figure 9, where we have plotted the rate arising from only the O atoms against the temperature. The rate arising from the oxygen molecules has been subtracted from the total rate. Below 1370 K this correction is insignificant, and at 1520 K it is roughly 33 percent of the total rate. It is evident from figure 9 that indeed there is little activation energy required for

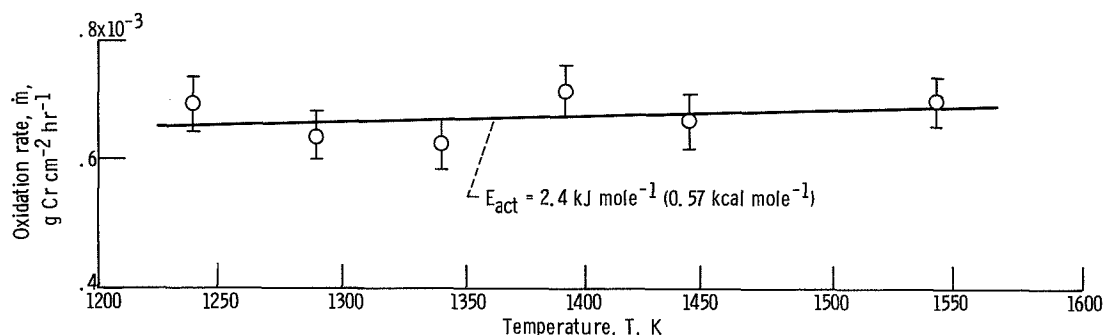
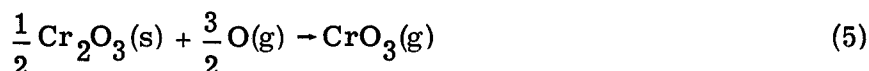


Figure 9. - Oxidative vaporization of Cr_2O_3 by oxygen atoms. Oxygen atom pressure, $P_0 = 0.39 \text{ N m}^{-2}$ ($3.8 \times 10^{-6} \text{ atm}$).

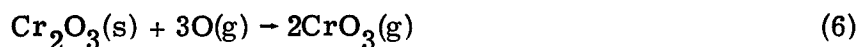
the reaction of O atoms with Cr_2O_3 in this temperature regime. A linear least-squares analysis of an Arrhenius plot of this data yielded an $E_{\text{act}} = 2.4 \text{ kJ mole}^{-1}$ (0.57 kcal mole^{-1}). This low activation energy for the O atom reaction is similar to the results obtained with the metals platinum (ref. 2) and molybdenum and tungsten (ref. 3).

We have investigated the effect of varying the O atom concentration on the rate in this temperature regime. The concentration of O atoms was lowered by removing the 5-percent N_2 from the oxygen stream. While only two concentrations were available by this technique, the runs could be cycled readily between the two O atom concentrations. The points presented represent the average of several runs.⁵ In addition, the origin represents a bona fide point.

The results at a temperature of 1320 K are presented in figure 10, where the rate is plotted against the 3/2 power of the partial pressure and of the collision flux of the O atoms. The results indicate that the reaction is 3/2 order with respect to O atoms. The 3/2 order is unusual because the reaction of O atoms with metals always exhibits first-order kinetics (refs. 2 and 3). In addition, O atom recombination on solid surfaces usually follows first-order kinetics (ref. 6). However, in this case the 3/2 order is predicted by the stoichiometry of the oxidative reaction:



It appears, therefore, that the rate-determining step must be quite complicated and involves the formation of an activated complex on the surface consisting of three oxygen atoms and a Cr_2O_3 moiety:



It is surprising that the activation energy for such a complex reaction should be as low as 2 kJ mole^{-1} (0.5 kcal mole^{-1}).

Comparison with thermodynamic predictions. - As in the reaction of Cr_2O_3 with molecular oxygen (ref. 5), the rate data can be compared with rates predicted from thermodynamic data. This comparison is presented in figure 11, where we have plotted the logarithm of the rate against the temperature. We have also included the comparison in molecular oxygen from reference 5 and have extrapolated these to 470 K by using a linear extrapolation of log rate against T^{-1} . The calculated and experimental rates in partially atomic oxygen are in qualitative agreement. Both indicate a marked enhancement in the oxidation rate and exhibit a maximum in the rate at intermediate temperatures. Never-

⁵The standard deviation of the mean of the individual runs was ± 4 percent.

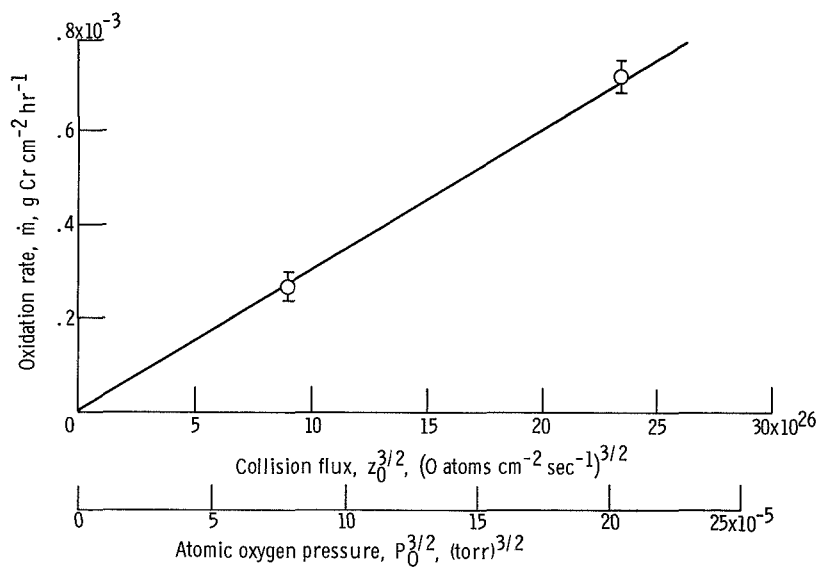


Figure 10. - Oxidative vaporization of Cr_2O_3 as function of $3/2$ power of the oxygen atom collision flux at 1323 K.

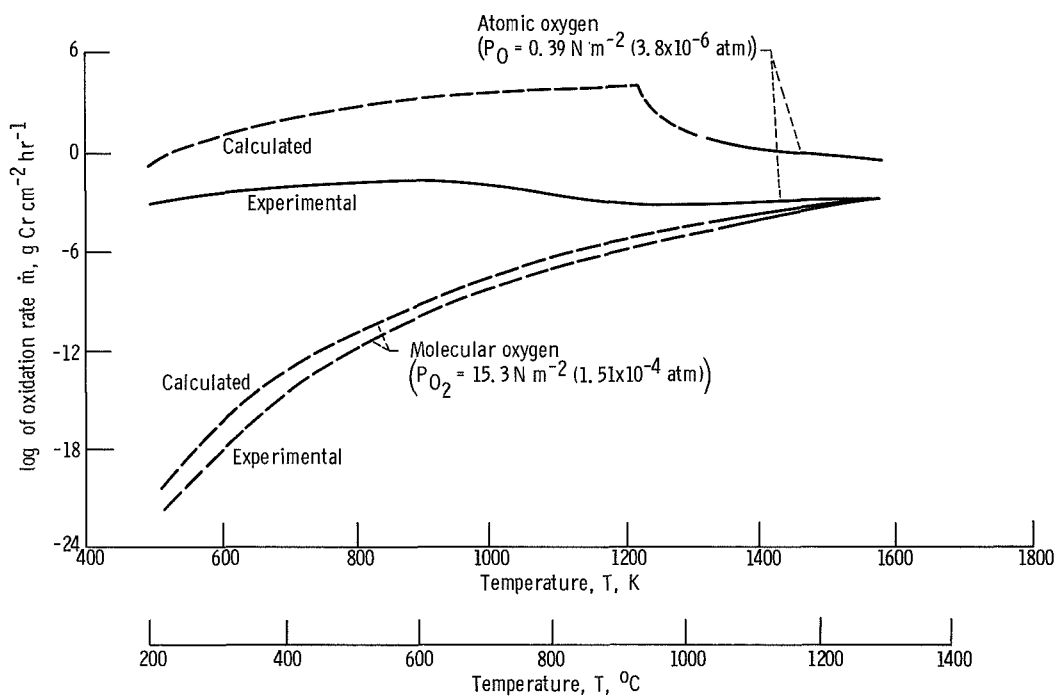


Figure 11. - Experimental and calculated rates of oxidative vaporization of Cr_2O_3 in partially atomic oxygen. (Dashed curves are extrapolated.)

theless, there is a large difference in the values of the rates⁶ and in the temperature at which the maximum occurs. Both of these factors depend on the concentration of O atoms on the surface of the Cr_2O_3 . We believe the disparity arises from the fact that the concentration of O atoms on the surface is much less than the equilibrium value corresponding to the gaseous partial pressure. This low oxygen atom concentration results from rapid recombination of the adsorbed O atoms on the hot surface. While it has been shown that Cr_2O_3 at room temperature has a very low recombination coefficient for O atoms (refs. 6 and 19), the recombination coefficient increases rapidly with increasing temperature (ref. 6).⁷ This relation might offer an explanation for the drop in rate at 820 K. However, we feel that destabilization of the CrO_3 polymers is a more plausible explanation because of the thermodynamic data presented in this report.

Enhancement in oxidation rate. - It is interesting to consider the enhancement in the rate of oxidation of Cr_2O_3 effected by this small concentration of O atoms in the gas phase. The enhancements have been calculated at different temperatures from the results given in figure 11 and are presented in figure 12. We give here the enhancement calculated from both the experimental and the calculated rates. The experimental enhancements are truly enormous at the lower temperatures, being 10^{20} at 470 K and 10^9 at 820 K. At 1270 K the enhancement is 100. Of course, with larger concentrations of O atoms, the enhancements would be even greater. In this respect, more valid values for the enhancements can be obtained by comparing the oxidation probabilities of the O atoms and of the O_2 molecules in the oxidative vaporization of Cr_2O_3 . Table I illustrates

⁶These experimental rate data in O atoms have not been corrected (as was done in ref. 5) for the fact that the temperature of the oxygen was not the same as that of the sample. The correction is insignificant in comparison to the discrepancy between the experimental and calculated rates.

⁷An oxygen atom recombination coefficient changing with temperature would affect the value of the energy of activation obtained for the data that we have presented in figs. 8 and 9. In fact, this relation may account for lack of linearity throughout the entire temperature range displayed by the data for reaction (2) presented in fig. 8. Certainly the recombination coefficient on Cr_2O_3 is increasing in this temperature range (ref. 6). This would have the effect of depressing the higher temperature data and may also indicate that the value of 33 kJ mole⁻¹ (8 kcal mole⁻¹) should be the preferred value for the energy of activation for reaction (2).

The data for reaction (3) presented in fig. 9 fall nicely on a straight line and yield a very reasonable value for the energy of activation. It appears that the oxygen-atom recombination coefficient on Cr_2O_3 in this temperature range is either constant or changes little.

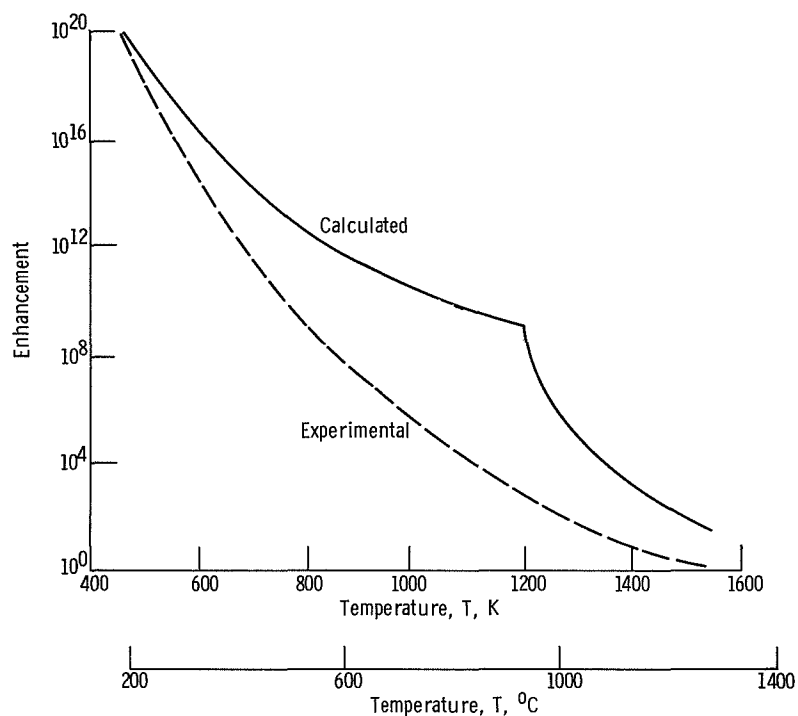


Figure 12. - Enhancement of oxidative vaporization of Cr_2O_3 in partially atomic oxygen. Experimental pressures: P_{O_2} , 15.3 N m^{-2} (1.51×10^{-4} atm); P_{O} , 0.39 N m^{-2} (3.8×10^{-6} atm).

TABLE I. - COMPARISON OF OXIDATION
PROBABILITIES OF O ATOMS AND O_2
MOLECULES IN OXIDATIVE
VAPORIZATION OF Cr_2O_3

Temperature, K	Oxidation probability		Enhancement, $\epsilon_{\text{O}}/\epsilon_{\text{O}_2}$
	Atomic oxygen, ϵ_{O}	Molecular oxygen, ϵ_{O_2}	
1270	2×10^{-3}	2.4×10^{-7}	8500
1370	↓	2.9×10^{-6}	690
1470		1.3×10^{-5}	150
1570		5.3×10^{-5}	38

such a comparison for the temperature range 1270 to 1570 K, where the analogous reactions (1) and (3) are occurring; that is, oxidation to the $\text{CrO}_3(\text{g})$ monomer is taking place. The ϵ_{O} for the O atoms is constant. The ϵ_{O_2} have been calculated from the smoothed data of reference 5. The enhancement varies from roughly 10^4 at 1270 K to 40 at 1570 K.

Oxidation of Chromium

A very interesting discovery of this work was the occurrence of the rapid, direct oxidative vaporization of chromium metal by O atoms in the region below 1070 K. The rates of oxidation of electropolished chromium in O atoms (lower solid curve of fig. 7) were independent of time, as one would expect for such a reaction. Below about 1070 K the chromium ribbons remained bright and shiny after a series of oxidations wherever they had been exposed to the O atoms, though some bright-green Cr_2O_3 was formed towards the ends of the ribbons near 1070 K. The rates were fairly reproducible and were generally about one-half the rates observed for Cr_2O_3 . The rates displayed the same peculiar dependence on temperature that the Cr_2O_3 rates did, and we explain this behavior on the same basis. The reaction occurring is represented by reaction (4); namely, $\text{Cr}(\text{s}) + \text{O}(\text{g}) \rightarrow (\text{CrO}_3)_n(\text{g})$, where $n = 3, 4$, and 5.

We have investigated the order of this reaction at a temperature of 723 K. The results are given in figure 13, where the rate of oxidative vaporization of chromium is

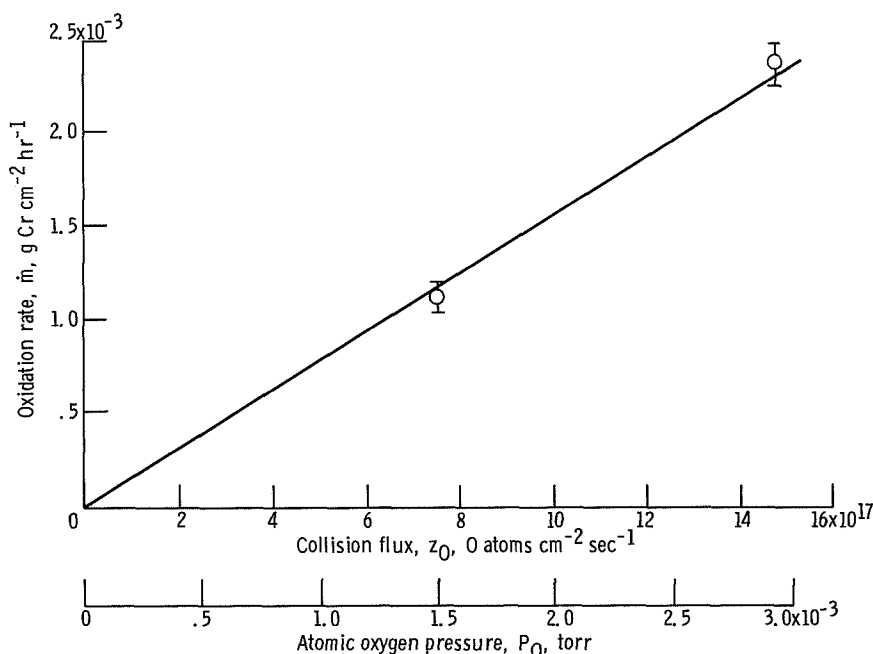
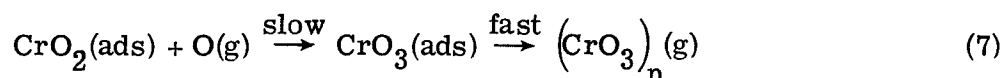


Figure 13. - Oxidative vaporization of chromium as function of oxygen atom collision flux at 723 K.

plotted against the partial pressure and the collision flux of O atoms. The results follow first-order kinetics quite nicely. The O atom concentration was varied as previously described. The points represent the average of several runs, and the origin again represents a bona fide point. The first-order kinetics for the reaction of chromium with O atoms is in agreement with the results found for the other metals. The rate-determining step is probably similar to that postulated by Fryburg for platinum, molybdenum, and tungsten (ref. 2); namely,



The oxidation probabilities of the O atoms in this reaction have been calculated and are presented in figure 7. Because the reaction is first order, the oxidation probability is equivalent to the "collision efficiency," which is defined as the fraction of O atoms

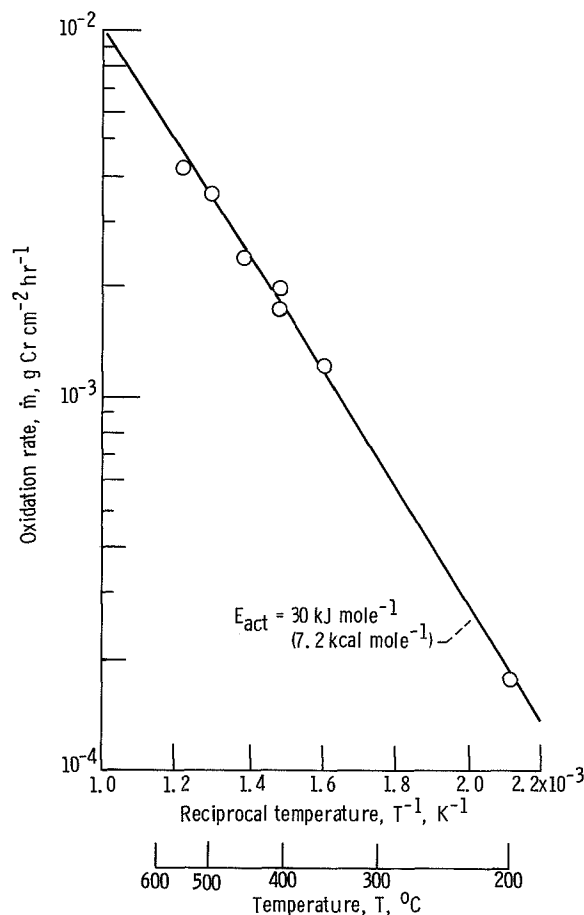
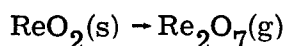
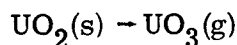
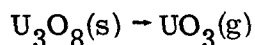
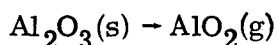
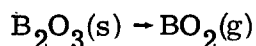


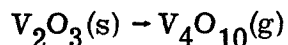
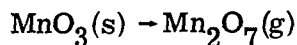
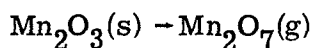
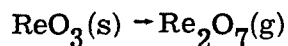
Figure 14. - Arrhenius plot of oxidative vaporization of chromium in partially atomic oxygen from 470 to 820 K. Atomic oxygen pressure, P_{O} , 0.39 N m^{-2} ($3.8 \times 10^{-6} \text{ atm}$).

striking the surface that react. The maximum value of the collision efficiency occurs at 823 K and is $\epsilon_O \approx 0.014$, that is, one O atom reacts in every 70 atoms that strike the chromium metal. This value may be compared with the collision efficiency ($\epsilon_O = 5 \times 10^{-6}$) of O atoms in the platinum metal oxidation (ref. 2) and with the oxidation probabilities reported for molybdenum and tungsten (ref. 3), which vary from about 0.1 to 0.5 depending on the temperature. It should be noted, however, that the chromium - O atom reaction occurs at noticeably lower temperatures than the reaction of the other metals. This lower temperature reaction results partly from the high volatility of CrO_3 down to 470 K; but it also indicates that the activation energy for the reaction must be low, as observed with the other metals. An Arrhenius plot of our rate data for electropolished chromium in the temperature range 470 to 820 K is presented in figure 14. A least-squares analysis of this data yields an activation energy of 30 kJ mole^{-1} ($7.2 \text{ kcal mole}^{-1}$). This is in good agreement with the values found by Rosner (ref. 3) for similar reactions of molybdenum and tungsten with O atoms; namely, 25 and 17 kJ mole^{-1} (6 and 4 kcal mole^{-1}), respectively. These results emphasize the fact that these metal - O atom reactions can occur at any temperature above which the oxide product is volatile. We have also shown in this report that the same is probably true for oxide - O atom reactions, in which a lower valent oxide can be oxidized to a higher valent, volatile oxide.

IMPLICATIONS

Based on the high reactivity of O atoms and the low activation energy found for the oxidative vaporization of Cr_2O_3 , we predict that an enhanced oxidation in O atoms should be exhibited by any oxide for which there exists a stable, gaseous oxide of high volatility with the metal in a higher valence state. Of course, the enhancement would occur only in the temperature and pressure range where the higher valent oxide was volatile and abundant. The following systems fulfill these criteria:





It is evident from this study that the high rate of removal of the so-called protective oxide Cr_2O_3 and the subsequent high rate of removal of underlying chromium metal by O atoms poses a serious problem in the selection of materials for reentry vehicles which experience high heating rates under conditions such that high O atom concentrations are present.

Our measurements on the chromium - atomic oxygen system have revealed some interesting phenomena and raised some interesting questions. More sophisticated methods, such as high-pressure mass spectrometry and high-temperature electron spectroscopic chemical analysis are required to pursue this study and should yield valuable information.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 11, 1974,
502-01.

APPENDIX - METHOD OF CONSTRUCTION OF THERMOCHEMICAL

DIAGRAMS AND SOURCES OF THERMODYNAMIC DATA

Thermochemical diagrams were constructed following the method outlined by Gulbransen and Jansson (refs. 14 to 18). Thermodynamic data for O(g), Cr(g), CrO(g), and CrO₂(g) were taken directly from Schick (ref. 20); the log K_p⁸ values for Cr₂O₃(s) were calculated from ΔG_f⁰ values given by Wicks and Block (ref. 21). Thermodynamic data for Cr₂(g) were taken from Kant and Strauss (ref. 22). The data for the condensed phase of CrO₃ (mp = 470 K) are given by Schick to 800 K. The values of log K_p to 1600 K were obtained by linearly extrapolating the low-temperature values given in Schick as a function of reciprocal temperature to 1600 K. For CrO₃(g), the values of log K_p were obtained by use of the relation:

$$\log K_{p, \text{CrO}_3(\text{g})} = \log P_{\text{CrO}_3(\text{g})} + \frac{1}{2} \log K_{p, \text{Cr}_2\text{O}_3(\text{s})} - \frac{3}{4} \log P_{\text{O}_2(\text{g})}$$

The values of log P_{CrO₃(g)} as a function of temperature and oxygen pressure were taken from the work of Kim and Belton (ref. 12) for the temperature range 1500 to 1800 K. The values of log K_{p, CrO₃(g)} at lower temperatures were obtained by linear extrapolation of the high-temperature values as a function of reciprocal temperature down to 500 K.

The mass spectrometrically determined vapor pressure data of Washburn (ref. 23) for the (CrO₃)₃, (CrO₃)₄, (CrO₃)₅, Cr₃O₇, Cr₄O₁₀, and Cr₅O₁₃ molecules over CrO₃(s) were used to obtain the necessary thermodynamic data for these molecules. The reliability of thermodynamic data derived from Washburn's measurements are based on the assumption that the complex chromium-oxygen molecules observed in the mass spectrometer were in equilibrium with the condensed-phase CrO₃ and with each other in the Knudsen cell source. Washburn's vapor pressure measurements covered the temperature range of 415 to 568 K. By combining his vapor pressures and heats of sublimation with our selected value⁹ of 17 kJ mole⁻¹ (4.0 kcal mole⁻¹) for the heat of melting ΔH_m

⁸Log K_p stands for the logarithm (to the base 10) of the equilibrium constant for the reaction of forming the given compound from its elements in their standard states.

⁹The selected value of ΔH_m(CrO₃) of 17 kJ mole⁻¹ (4.0 kcal mole⁻¹) was obtained by consideration of the values listed by Coughlin (ref. 24) of 15.8 kJ mole⁻¹ (3.77 kcal mole⁻¹), Schick's (ref. 20) estimate of 22.4 kJ mole⁻¹ (5.36 kcal mole⁻¹), and the experimental value of 16 kJ mole⁻¹ (3.9 kcal mole⁻¹) recalculated from the data given by McDonald and Margrave (ref. 25).

of $\text{CrO}_3(\text{s})$, values were obtained for the heats of vaporization and for the vapor pressures of the chromium-oxygen molecules over $\text{CrO}_3(\text{l})$ at temperatures above 470 K. These vapor pressures were extrapolated linearly as a function of reciprocal temperature to 1600 K. The $\log K_p$ values for the molecules were obtained by using expressions of the type

$$\log K_{p, (\text{CrO}_3)_3(\text{g})} = \log P_{(\text{CrO}_3)_3(\text{g})} + 3 \log K_{p, \text{CrO}_3(\text{l})}$$

and

$$\log K_{p, \text{Cr}_3\text{O}_7(\text{g})} = \log P_{\text{Cr}_3\text{O}_7(\text{g})} + \log P_{\text{O}_2(\text{g})} - \log P_{(\text{CrO}_3)_3(\text{g})} + \log K_{p, (\text{CrO}_3)_3(\text{g})}$$

from 500 to 1600 K. Washburn found that the oxygen partial pressures in his Knudsen cell were a factor of 10^{-10} less than that expected from thermodynamic calculations. Therefore, in order to calculate the equilibrium O_2 partial pressures at the various temperatures, we assumed that CrO_3 vaporizes congruently and that the sum of the number of moles of Cr_3O_7 , Cr_4O_{10} , and Cr_5O_{13} equals the number of moles of $\text{O}_2(\text{g})$. The values of $\log K_p$ for all the species under consideration are given from 500 to 1600 K in table II. The not-well characterized $\text{CrO}_2(\text{c})$ phase was not considered in the present treatment because calculations showed that even higher oxygen pressures were needed to stabilize this phase than were needed to stabilize CrO_3 .

The partial vapor pressures of the molecular species were calculated by considering the expression for the equilibrium constant in terms of the activities of reactants and products for the appropriate chemical reactions, and by using the relation

$$\log K_{\text{reaction}} = \sum \log K_{p, \text{products}} - \sum \log K_{p, \text{reactants}}$$

TABLE II. - EQUILIBRIUM CONSTANTS FOR CHROMIUM-OXYGEN SYSTEM

Temperature, K	log K _p for formation of species from reference state, Cr(s) and O ₂ (g)													
	O(g)	Cr ₂ O ₃ (s)	CrO ₃ (l)	Cr(g)	Cr ₂ (g)	CrO(g)	CrO ₂ (g)	CrO ₃ (g)	(CrO ₃) ₃ (g)	(CrO ₃) ₄ (g)	(CrO ₃) ₅ (g)	Cr ₃ O ₇ (g)	Cr ₄ O ₁₀ (g)	Cr ₅ O ₁₃ (g)
500	-22.939	105.04	48.704	-33.610	-56.595	-16.090	9.821	31.03	140.51	188.84	236.57	135.57	184.87	232.64
600	-18.547	85.253	38.893	-26.723	-45.490	-12.472	9.403	25.23	112.56	150.71	188.70	109.21	148.66	186.79
700	-15.449	71.138	31.943	-31.813	-37.582	-9.896	7.382	21.10	92.78	123.71	154.80	90.64	123.03	154.34
800	-13.101	60.566	26.772	-18.137	-31.669	-7.973	6.609	18.01	77.82	103.30	129.18	76.59	103.65	129.80
900	-11.272	52.343	22.75	-15.284	-27.086	-6.483	6.002	15.60	66.21	87.47	109.30	65.69	88.62	110.76
1000	-9.806	45.775	19.53	-13.006	-23.434	-5.296	5.512	13.68	56.93	74.80	93.40	56.98	76.59	95.53
1100	-8.606	40.382	16.90	-11.147	-20.459	-4.331	5.105	12.10	49.34	64.44	80.39	49.85	66.75	83.07
1200	-7.604	35.915	14.71	-9.604	-17.990	-3.532	4.762	10.80	43.01	55.80	69.55	43.90	58.55	72.69
1300	-6.755	32.118	12.85	-8.302	-15.914	-2.862	4.466	9.689	37.65	48.49	60.37	38.87	51.61	63.90
1400	-6.027	28.888	11.26	-7.191	-14.143	-2.292	4.208	8.750	33.06	42.23	52.51	34.56	45.67	56.37
1500	-5.395	26.044	9.88	-6.233	-12.620	-1.803	3.980	7.912	29.08	36.80	45.69	30.83	40.51	49.85
1600	-4.842	23.603	8.67	-5.398	-11.296	-1.380	3.776	7.204	25.60	32.05	39.73	27.56	36.00	44.14

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